



Primary Particles Generated by the Combustion of Heavy Fuel Oil and Coal

Review of Research Results
from EPA's National Risk
Management Research
Laboratory

Prepared for

**Office of Research and
Development**

Prepared by

National Risk Management
Research Laboratory
Research Triangle Park, NC 27711

Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

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Review of Research Results from EPA's National
Risk Management Research Laboratory

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Abstract

Researchers at the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development (ORD) have conducted a series of tests to characterize the size and composition of primary particulate matter (PM) generated from the combustion of heavy fuel oil and pulverized coal. These tests, conducted at ORD's National Risk Management Research Laboratory (NRMRL) in Research Triangle Park, NC, burned four heavy fuel oils and seven coals in three small combustion systems and measured size distributions and composition of the particles formed in the combustion process. The research found that, for heavy fuel oils, particle composition and size are dependent upon the combustion environment in the combustor. In the coolest test unit, unburned carbon in the fly ash was very high (70-90% by mass), and PM mass emissions were also high, with the majority of the mass being in the coarse ($> 2.5 \mu\text{m}$ in aerodynamic diameter) size range. In the hottest test unit, the PM mass emissions were approximately 50% of those from the coolest unit, unburned carbon levels were approximately zero, and the entire PM mass was in particles smaller than $1 \mu\text{m}$ in aerodynamic diameter. For coal, the NRMRL research identified a previously unreported trimodal particle size distribution, with an ultrafine ($\sim 0.1 \mu\text{m}$ in aerodynamic diameter) mode, a coarse ($> 5 \mu\text{m}$ in aerodynamic diameter) mode, and a central mode of particles between 2 and $4 \mu\text{m}$ in aerodynamic diameter. The central mode has a composition similar to the coarse mode, but significantly different from the ultrafine mode. It is hypothesized that the composition of the ultrafine coal particle fraction is similar to the fine particle fraction in heavy fuel oil, which has been shown to generate increased toxicological responses following pulmonary exposure in laboratory animals. These findings may have implications for future PM control strategies, given the influence of operating conditions and the water-soluble composition of the smallest particle fractions of PM from metal-bearing fossil fuels

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Section 1

Executive Summary

In 1997, the U.S. Environmental Protection Agency (EPA) promulgated revisions to the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM) to add primary standards for ambient concentrations of PM smaller than 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$). The motivation for this revision was the body of epidemiological studies that associated elevated concentrations of ambient $\text{PM}_{2.5}$ with increases in human mortality and morbidity. To support the implementation of the revised standard, the National Risk Management Research Laboratory (NRMRL) began a series of tests to characterize the particles directly emitted from the combustion of heavy fuel oils and pulverized coals. This research was initially intended to provide data for improved emission inventories. During the course of the program, the characterization data for inventory improvement has been generated, and a portion of the research has also evolved to include a series of toxicological studies in collaboration with EPA's National Health and Environmental Effects Research Laboratory (NHEERL).

The main focus of this report is the physico-chemical characterization of primary PM from fossil fuel combustion. This work was conducted at NRMRL's combustion research facilities in Research Triangle Park, NC, using several of the Laboratory's research combustors. Using state of the art measurement systems, NRMRL researchers have identified several characteristics of combustion-generated primary particles and have associated these characteristics with fundamental particle formation mechanisms to allow these results to be extended to other high temperature systems. The key findings of this research are provided below.

The collaborative NRMRL-NHEERL research is addressed briefly here, but is currently on-going and outside the scope of this report.

Findings

The key findings from NRMRL's research to characterize primary PM generated from the combustion of heavy fuel oil and pulverized coal are:

- Modest changes in combustion conditions, such as slight reductions in excess air and reducing oil feed temperature, do not significantly change the mass emissions of PM from heavy fuel oil combustion.
- Significant changes in combustion conditions due to different combustor designs result in substantial changes in PM characteristics and mass emissions when burning heavy fuel oil.
- Incomplete combustion of the carbon in the heavy fuel oil results in the formation of large ($>20 \mu\text{m}$ diameter) particles that contribute substantially to the total PM mass emission rates for certain boiler designs.

- The submicron ($<1\ \mu\text{m}$ in aerodynamic diameter) particles contain metals and sulfur that are largely in water soluble form, in contrast to the supermicron ($>1\ \mu\text{m}$ in aerodynamic diameter) fraction of particles that contains less soluble thiophenic sulfur and less soluble metal species.
- A previously unreported particle mode between 0.8 and 2.0 μm contributes considerably to the mass emissions of $\text{PM}_{2.5}$ from the combustion of pulverized coal.
- The composition of particles in the “fine fragmentation” mode between 0.8 and 2.0 μm is similar to that of coarse mode particles from pulverized coal combustion. This suggests that these 0.8-2 μm particles are formed by coarse ash particles that fragment during the combustion process. The composition also suggests that these particles will have metals with relatively low water solubility and possibly relatively low bioavailability.
- The ultrafine ($<0.1\ \mu\text{m}$ in aerodynamic diameter) fraction of coal-generated particles has composition similar to that of the ultrafine mode of particles from heavy fuel oil combustion, suggesting that the pulmonary toxicity of ultrafine particles from coal combustion may be similar to the heavy fuel oil ultrafine particles.

Implications

Particle composition varies considerably with size, with potentially significant implications for particle toxicity. NRMRL’s research, consistent with previous work, has identified significant variation in particle composition as a function of particle size. The submicron (especially the ultrafine) particle fractions were consistently composed of metal and other sulfates that are highly water soluble, meaning that they are more likely to interact with biological tissues when inhaled. The formation mechanisms that generate these particles govern both size and composition. Therefore, the question of whether size or composition plays a dominant role in causing adverse health effects may be inappropriate, since the two (size and composition) cannot be separated in real-world systems. It may be more relevant to focus on particles with similar formation processes rather than on particles with specific characteristics that cannot be naturally separated. In short, multiple mechanisms are involved in the formation of $\text{PM}_{2.5}$ from combustion sources, and these mechanisms will directly impact the role of particles in causing adverse health effects.

The design and operation of a source can result in significant changes in the physico-chemical and toxicological characteristics of the particles generated. This finding has scientific and, potentially, regulatory implications. In the context of toxicological research, more emphasis needs to be placed on how particle samples are generated and collected. PM toxicological studies often do not adequately describe the source characteristics (including system design), the conditions at which the system was running, or the methods used to extract particle samples. PM from heavy fuel oil, as demonstrated here, is not a homogeneous material with consistent characteristics. In order to develop an adequate understanding of the health effects associated with PM and

the causal mechanisms leading to those effects, studies must provide enough information to allow the reader to understand the representativeness of the particles used in the tests.

From a regulatory perspective, these results may eventually be used to identify source types that have the potential for emitting particles having characteristics closely associated with health risk. As additional understanding is gained regarding links between health effects and particle characteristics, it may someday be possible to develop regulatory approaches to reduce PM emissions from a more limited range of source types, or to minimize emissions of particles with certain characteristics. If enough information on adverse health effects due to water-soluble ultrafine particles is developed, for instance, limits on emissions of these particles may replace or supplement limits on total mass emissions.

Future Directions

NRMRL's research to characterize primary particles from the combustion of pulverized coal and heavy fuel oils has been completed. There remain numerous research opportunities in the broader area of combustion-generated particles, which will be followed as appropriate. Immediate efforts will focus on characterizing emissions from small off-road diesel engines, which will involve more organic analysis as compared to the significant levels of inorganic analysis conducted for the previous studies. Several efforts associated with the collaborative studies linking the physico-chemical properties of combustion-generated particles to measures of toxicity during direct inhalation exposures will continue. This area of work shows considerable promise for generating data that can be used to better understand the links between sources and adverse health effects.

The capabilities developed during the work described in this report will continue to generate state of the art research. NRMRL's flexible and unique facilities, in combination with ORD's on-site expertise, provide unique opportunities for leading edge multidisciplinary research in PM, air toxics, and other air programs.

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Section 2

Introduction

In 1997, the U.S. Environmental Protection Agency (EPA) promulgated revisions to the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM) to add primary standards for ambient concentrations of PM smaller than 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$). The motivation for this revision was the body of epidemiological studies that associated elevated concentrations of ambient $\text{PM}_{2.5}$ with increases in human mortality and morbidity. Although the specific mechanisms of health damage that resulted in these associations had not been demonstrated, numerous toxicological studies provided considerable evidence for several plausible mechanisms. Several of the particle characteristics hypothesized to cause at least part of these adverse health effects are typical of particles formed during the combustion of metal-containing fossil fuels such as coal and heavy fuel oil.

As part of the broader effort by EPA's Office of Research and Development (ORD) to provide scientific tools and information to support implementation of the new standard, the National Risk Management Research Laboratory (NRMRL) initiated a study to more fully characterize the primary particles generated from fossil fuel combustion. NRMRL's facilities and expertise developed for studies of waste incineration and hazardous air pollutant characterization provided an opportunity for ORD to quickly generate data on emissions rates, particle size distributions (PSDs), and composition as well as information on particle formation mechanisms in fossil fueled combustion systems. Based on available data, a relatively modest program was anticipated to develop data on PM from fossil fuels, beginning with heavy fuel oils and later moving to coals.

As the program developed, opportunities for collaboration with ORD's National Health and Environmental Effects Laboratory (NHEERL) and unexpected results combined to stretch the program beyond the originally anticipated scope. The research has met its original goals, and the evolution of the program has resulted in clearer insights into particle formation processes while expanding ORD's capabilities to address complex, multidisciplinary environmental problems.

This document will provide a summary of the scientific motivations for this research, briefly describe how the work was conducted and the quantitative results were obtained, discuss the broader significance of these results, and identify some potential future work that may be derived from these efforts.

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Section 3

Background

The fundamental motivation for this work is the epidemiological evidence that associates adverse human health effects with increased levels of ambient PM concentrations, and EPA's promulgation of a NAAQS for PM_{2.5}. A number of studies have linked increases in ambient concentrations of PM to both short-term (acute) and long term (chronic) adverse human health effects, including premature death. These epidemiological studies examined statistics on mortality and morbidity as measured by data such as hospital admissions and sought to identify possible correlations with ambient air pollution data. In general, the epidemiological studies concluded that there is, in fact, a direct correlation between ambient fine PM concentrations and increases in human mortality and morbidity (Dockery et al. 1993, Burnett et al. 1995, Schwartz and Morris 1995, Lippmann et al. 2000, Samet et al. 2000). These studies were summarized by EPA (Bachmann et al. 1996, U.S. EPA 1996) and reviewed by EPA's Clean Air Science Advisory Committee (CASAC), both of which determined there was sufficient evidence linking ambient fine PM concentrations and acute adverse cardiopulmonary health effects to warrant a revision of the previously existing standard (Wolff 1996). In July 1997, EPA revised the PM NAAQS to add to the existing standards for PM smaller than 10 µm in aerodynamic diameter (PM₁₀) two primary standards for PM_{2.5}, a 65 µg/m³ 24-hour average and a 15 µg/m³ annual mean, while retaining the previous 24-hour and annual PM₁₀ standards of 150 and 50 µg/m³, respectively (Federal Register 1997). Although the PM₁₀ standards were challenged in court and remanded to EPA for modification (U.S. Supreme Court 2001), the fundamental purpose of the standards—to reduce ambient concentrations of specific size fractions of PM for the purpose of protecting human health and the environment—has not changed.

Toxicological Studies

Numerous theories have been proposed to explain the mechanisms by which exposure to ambient particles causes adverse health effects. Among the particle characteristics that have been suggested as playing significant roles in the causal mechanisms are total particle mass; particle acidity, morphology, number, and/or size; presence of biogenic materials, organic compounds, oxidants, or transition metals; or interaction with other pollutants in the atmosphere. Studies of the effects of these different particle characteristics have been, and are currently being, conducted in clinical human exposure studies, studies of laboratory animals exposed to particles with different characteristics (*in vivo* studies), and biochemical studies of the response of cells to different compounds found in PM_{2.5} (*in vitro* studies). Of particular interest here are a series of studies that examined the effects of PM generated by the combustion of fossil fuels in stationary sources.

Research conducted at NHEERL showed that laboratory animals exposed to fine PM generated from the combustion of fossil fuels demonstrated significant adverse health

impacts. This research concluded that a major factor leading to these adverse health impacts was the amount of water-soluble transition metals such as copper (Cu), iron (Fe), nickel (Ni), vanadium (V), and zinc (Zn) present in the particles (Dreher et al. 1996a, 1996b, 1997; Hatch et al. 1982, 1985). Other, more recent, work has also indicated that pulmonary exposure to transition metals leads to adverse health effects through a number of different mechanisms including changes in cardiac function (Lighty et al. 2000, Fernandez et al. 2000, Godleski et al. 2000).

Particle size has also been proposed as playing a significant role in causing adverse health effects. Particles smaller than 0.1 μm in aerodynamic diameter (ultrafine particles) can have a greater biological effect than an equal mass of larger particles of the same substance. Ultrafine particles can be deposited deep in the lungs where they may be retained. Furthermore, ultrafine particles can pass through cells lining the lung, and their higher surface area (compared to an equal mass of larger particles) can result in a faster release of toxic compounds that may be associated with the particles (Oberdörster et al. 1995, Kuschner et al. 1997, Baggs et al. 1997).

Health damage has also been found to occur at significantly higher rates after exposure to particles on which acid or organic compounds have condensed compared to damage caused by exposure to any of the components by themselves. Particles on which sulfuric acid had condensed caused the same effect on lung capacity as a ten-fold higher dose of sulfuric acid alone in the form of a respirable mist. The level of this effect also depended upon the type of particle, since the acid could react with particle constituents to mitigate the effects (Amdur et al. 1986).

In summary, substantial evidence indicates that the particles containing transition metals, ultrafine particles, or acid aerosols are of importance to the issue of PM-related health effects. Each of these characteristics is associated with at least a fraction of the particles formed by the combustion of heavy fuel oils and coals.

Ambient Particles

Ambient particles are a mix of *primary* and *secondary* particles. Particles formed in combustion processes are considered to be *primary* because they are emitted directly from the exhaust in particulate form. Primary particles also include those particles formed from the physical nucleation or condensation of compounds that are in the vapor phase in the exhaust, but quickly nucleate or condense at ambient temperatures. In contrast, *secondary* particles are formed when vapor phase compounds chemically react in the ambient atmosphere to form particles. These particle-forming reactions often occur many miles downwind of the source of the precursor gases.

A majority of the fine particle mass in the ambient atmosphere is in the form of secondary nitrates and sulfates formed from precursor gases, sulfur dioxide (SO_2) and nitrogen oxides (NO_x). The percentage of SO_2 and NO_x that form solid secondary

particles varies by location and is influenced by factors such as local meteorology and composition of the air mass (including presence of water as either humidity or droplets, oxidants such as ozone, ammonium ions, and other pollutants or biogenic compounds). A considerable fraction (25-50%) of the total ambient PM mass across the United States is composed of these compounds (U.S. EPA 1996). Other constituents include organic carbon (condensed organic compounds and secondarily formed organic aerosols), elemental carbon (soot or other unburned carbon from combustion sources), particles of geological origin such as wind-blown dust from agricultural or construction activities, and inorganic compounds such as trace metals from the combustion of metal-containing fuels. Figure 1 illustrates representative compositions of ambient PM_{2.5} in the Eastern and Western United States (U.S. EPA 1996).

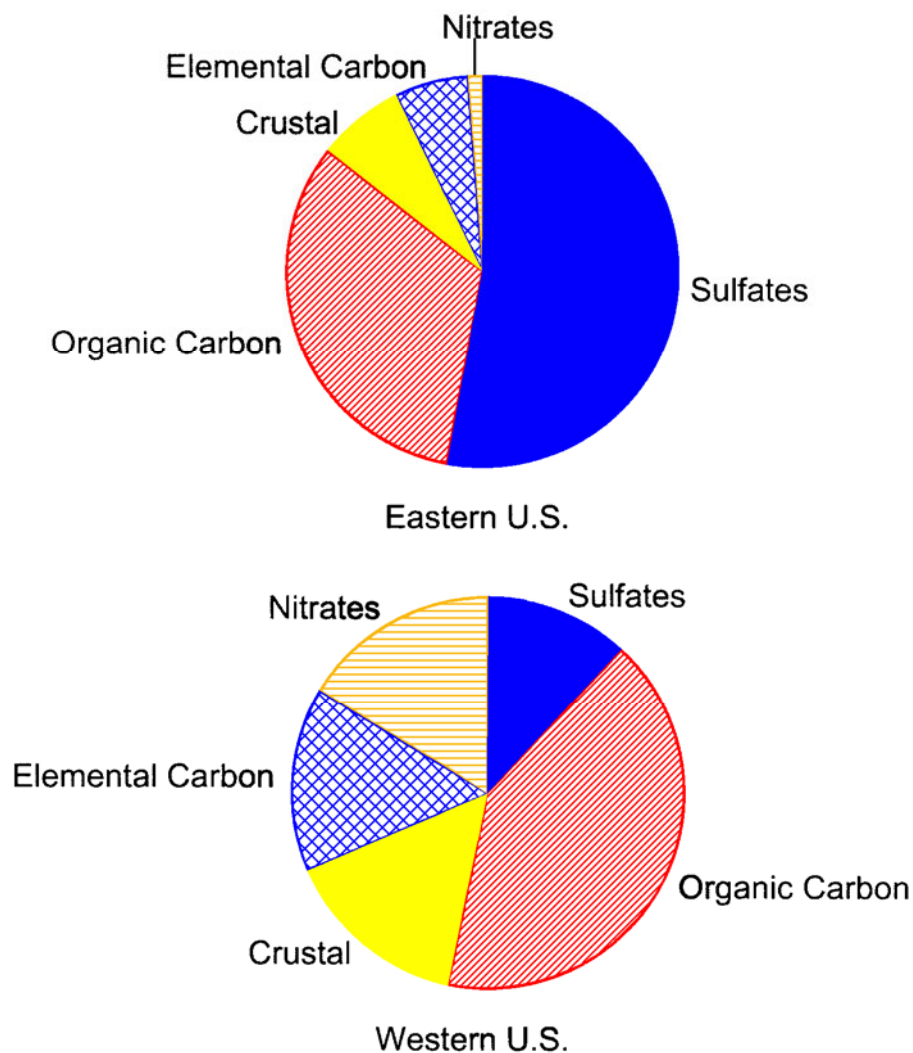


Figure 1. Composition of ambient PM_{2.5} in the Eastern (top) and Western (bottom) United States (U.S. EPA 1996).

Generally, ambient concentrations of primary particles from fossil fuel combustion are very low. Typical fractions of transition metals in ambient particle samples are 5% or less of the total sample mass. Nevertheless, these particles remain of interest for at least two reasons. First, it is unclear what the effects of long-term exposures to ambient concentrations of these compounds are, given the evidence that they are bioactive (based on testing at much higher concentrations than in the ambient environment). Second, it is not clear what the effects of these compounds may be in combination with sulfates, nitrates, and other ambient PM constituents.

Sources of PM

Much of the current information on sources of primary $PM_{2.5}$ is derived from existing emission inventories for PM_{10} combined with data on size distributions to estimate $PM_{2.5}$. Direct measurement of $PM_{2.5}$ emissions is, therefore, important to improving the accuracy of inventory estimates.

Figure 2 shows the relative amounts of directly emitted $PM_{2.5}$ in the U.S. in 1998. Wood

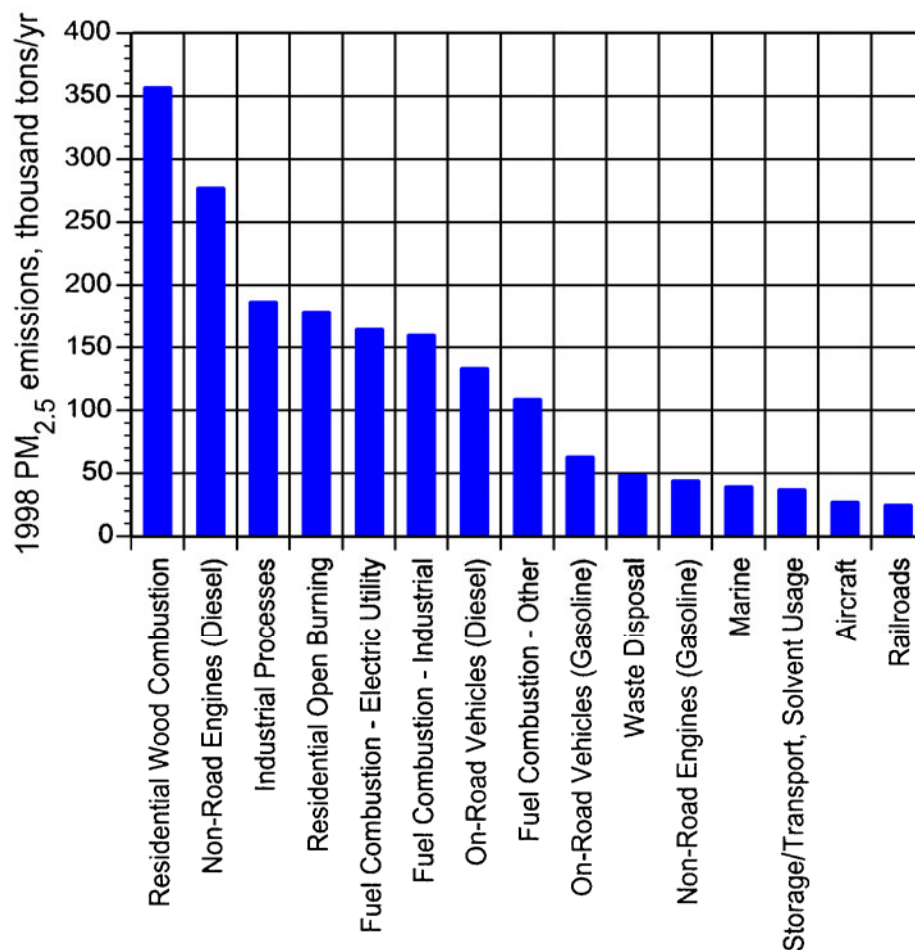


Figure 2. Major sources of Directly emitted $PM_{2.5}$ in the U.S. in 1998 (U.S. EPA 2000).

combustion from the residential sector is the largest source of primary PM_{2.5} (U.S. EPA 2000). Point source emissions of primary PM_{2.5} from fossil fuel combustion remain of considerable interest even though they do not emit the greatest amount of PM_{2.5} mass. Of most interest within this broad category are sources that use coal or heavy fuel oils. This is because of the presence of metals in the emissions and the relatively large size of the sources. Control of these large stationary sources is often more cost effective than control of smaller, more dispersed sources.

Coal and heavy fuel oils are used primarily in industrial and utility boilers to generate steam for process heat and electricity generation (see Figure 3). Coal use is heaviest in Texas and the Ohio River Valley, but is much more evenly distributed across the country than is heavy fuel oil use. Over 90% of coal is consumed by utilities in the generation of electricity, with a much smaller amount of electricity being generated from the combustion of heavy fuel oil. Heavy fuel oil is also used in utility and industrial plants and to a smaller extent in the transportation sector, almost entirely in ocean-going ships (U.S. Department of Energy 2000a, b, c). Heavy oil use largely occurs in states where the fuel can be transported by ship or barge or where there are local oil resources that can be used near the production sites (U.S. Department of Energy 2000b).

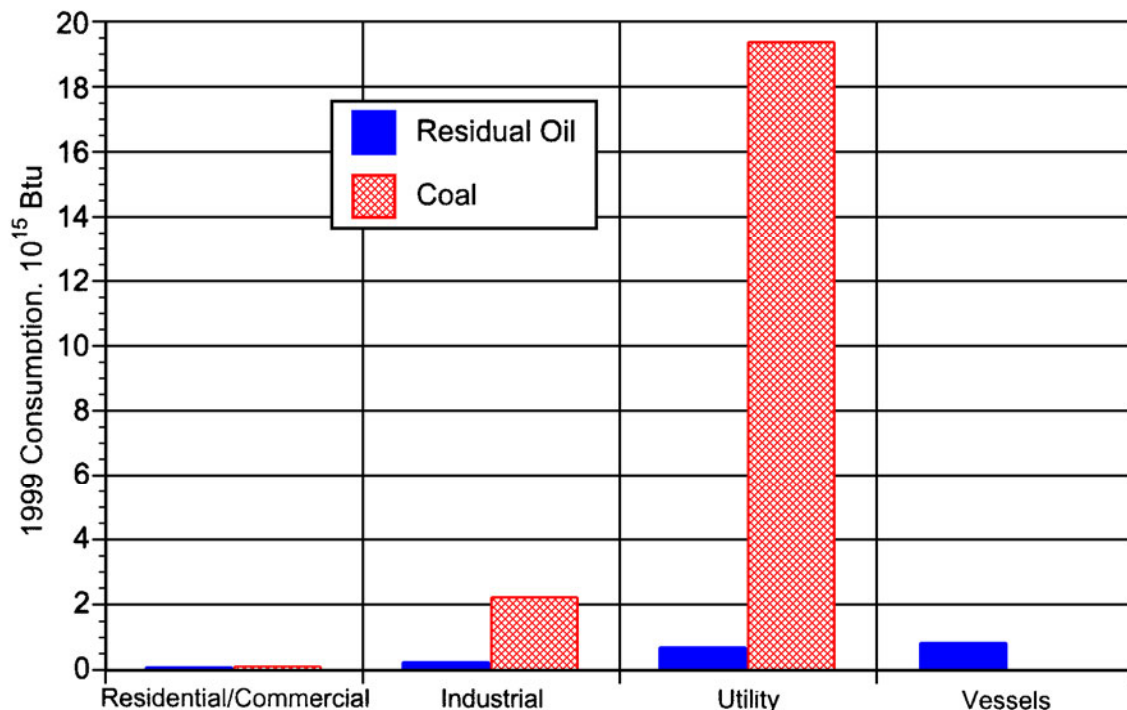


Figure 3. 1999 consumption of coal and residual oil in the U.S. by sector (U.S. Department of Energy, 2000a, b).

Previous Studies Characterizing Fossil Fuel Particles

There has been considerable work to characterize PM generated by the combustion of fossil fuels, particularly pulverized coal (Linak and Wendt, 1994). The focus of much of this previous work has been the prediction of ash composition for control of corrosion, fouling, slagging, and other adverse effects on combustor materials and heat transfer surfaces (Raask 1985). The fundamental particle formation and evolution mechanisms described in these studies are directly applicable to environmental investigations.

Particle Formation in Coal

Particles are generated during the combustion of pulverized coal through several different mechanisms that determine not only particle size but also the composition of the particles. In coal, 90-98% of the particle mass exiting the furnace is inorganic material that was present in the original fuel. The inorganic material may exist in the coal in several ways, ranging from tightly bound within the combustible organic material to distinct particles of inorganic matter (Gluskoter 1978). In the high temperatures of the combustion zone, the inorganic material may remain relatively intact, melt and form relatively large (1-30 μm) liquid droplets, or vaporize. The path depends upon the specific compound, how it is present in the fuel, the temperature, and the concentrations of other compounds in the combustion zone. In general, approximately 95% of the inorganic material present in coal does not vaporize.

Work by Gallagher et al. (1990), Flagan and Taylor (1981), Markowski et al. (1980), Neville et al. (1982, 1983), Okazaki et al. (1983), and Quann et al. (1982) typify the investigations that identified the governing mechanisms of particle formation in coal combustion systems and their effect on particle size and composition, particularly trace metal composition. These mechanisms are discussed briefly below.

Inorganic species that vaporize may undergo complex chemical reactions depending on the temperature and presence of other species. As a result of chemical reaction or falling temperatures, partial pressures approach and exceed critical supersaturation pressures, causing the inorganic species to either homogeneously nucleate and grow to form a submicron aerosol in the range of 0.01 to 0.05 μm in diameter or to heterogeneously condense on existing particle surfaces. Because submicron particles typically offer the major fraction of the available surface area, condensation tends to result in an enrichment of the inorganic vapor phase elements in the submicron particle fraction. Nucleation and coagulation also enrich the submicron particle fraction in vaporized elements, since these processes form particles that are smaller than 1 μm in diameter. Thus, the submicron and ultrafine particle size fractions can contain significantly higher percentages of those elements that pass through a vapor phase, compared to the larger particles that are not formed by nucleation or condensation processes.

Because growth by collision and coagulation with other particles is directly dependent on the number concentrations of the available particles, nuclei tend to grow very quickly for

a short time (1 to 5 s) and then, as number concentrations fall, particle growth slows considerably, causing the aerosol to accumulate into a mode between 0.05 to 0.5 μm diameter. Additional coagulation between nuclei and the larger accumulation mode particles does not noticeably affect the particle size distribution (PSD) because of the relatively small incremental mass added during each coagulation event.

In general, then, the results of previous investigations demonstrated that inorganic material, especially metals, can partition to different particle sizes due to the mechanisms governing particle formation in high temperature reactive processes such as coal combustion.

Particle Formation in Fuel Oil

Although the fundamental particle formation processes during the combustion of heavy fuel oils are the same as those for pulverized coal, there are distinct differences between the two fuels. In contrast to coals, oils do not typically contain significant extraneous or included mineral matter. The metals in heavy fuel oils are generally inherently bound within the organic molecule, which may be the case for only a small portion of the metals in higher rank coals. Unlike coal, interactions between volatile metal species and non-volatile minerals within the heavy fuel oil droplet are much less likely in heavy fuel oils. Typical fuel oils contain Fe, Ni, V, and Zn, in addition to aluminum (Al), calcium (Ca), magnesium (Mg), silicon (Si), and sodium (Na). Transition metals [Fe, manganese (Mn), and cobalt (Co)] and alkaline-earth metals [barium (Ba), Ca, and Mg] may also be added for the suppression of soot (Bulewicz et al. 1974) or for corrosion control (Feldman 1982).

Hersh et al. (1979), Piper and Nazimowitz (1985), and Walsh et al. (1991) showed that, in contrast to pulverized coal, the majority of the sampled fly ash mass from residual fuel oil combustion in power plants is likely to lie below 1 μm in diameter, although larger particles can form with poor carbon burnout. Furthermore, Walsh et al. (1991) have shown that Fe, Mg, and Ni are concentrated at the center of the submicron particles, while Na and V are associated with a "halo of sulfate residue." Bacci et al. (1983) found substantial enrichment of both Ni and V in the submicron particle size fraction of samples collected at a large oil-fired power plant. Walsh et al. (1994) indicated similar behavior for Ni and V. Again, these results demonstrate the compositional differences between coarse and fine PM fractions due to the mechanisms governing particle formation in fossil fuel combustion systems. However, none of these data showed detailed PSDs in the submicron range or provided *in-situ* measurements of the coarse (supermicron) mode.

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Section 4

Particle Characterization Research at NRMRL

With these results representing the state of the science at the inception of the NRMRL PM program, NRMRL researchers began a project to characterize PM generated by the combustion of heavy fuel oil. Heavy fuel oil was chosen because less research had been done on this fuel than on coal and because of its high transition metal content. In addition, heavy fuel oil is also often easier to burn than pulverized coal, and the fundamental mechanisms governing particle formation could be more easily studied than if coal were used. Even though heavy fuel oil use is much lower than coal use, the broader applicability of findings associated with particle formation in systems burning fuels containing transition metals (including both heavy fuel oil and coal) made heavy fuel oil an attractive first step in the research program.

Thus, initial work at NRMRL was proposed to provide accurate information on the mass emissions rate and size-specific composition of PM generated during the combustion of fossil fuels, with the intent of testing heavy fuel oil followed by pulverized coal. As the project progressed, the research expanded to incorporate a collaborative effort between NRMRL and NHEERL and incorporated data from other test programs, as appropriate, to allow the broadest possible evaluation of PM generated from fossil fuel combustion. This section will discuss the equipment and instrumentation used in the research program and the evolution and results of the characterization studies.

Experimental Equipment

NRMRL's experimental work was conducted at EPA facilities in Research Triangle Park, NC, using several different combustion systems and a range of instruments and methods for measuring particle size distributions and composition. NRMRL's variety of combustion equipment allowed the research to generate data simulating the behavior of a range of commercial and industrial systems using several different liquid and solid fuels.

Four combustors were used in NRMRL's PM characterization experiments: a firetube package boiler, a refractory-lined horizontal tunnel furnace, a waterwall package boiler simulator, and refractory-lined vertical (down-fired) tunnel furnace. Each unit has characteristics that simulate different types of industrial combustion systems and that result in somewhat different particle characteristics.

Initial experiments were conducted using NRMRL's North American firetube package boiler (NAPB), which is a practical heavy fuel oil combustion unit of a design used in commercial, institutional, and small industrial applications. A schematic of the NAPB is shown in Figure 4. In a firetube boiler, the hot combustion gases generated by the flame pass through tubes surrounded by water, which then generates low pressure steam for use in space and water heating and light process needs. The NAPB is rated at 2.5×10^6 Btu/hr (732 kW), and is capable of firing natural gas and No. 2 through No. 6 fuel oils.

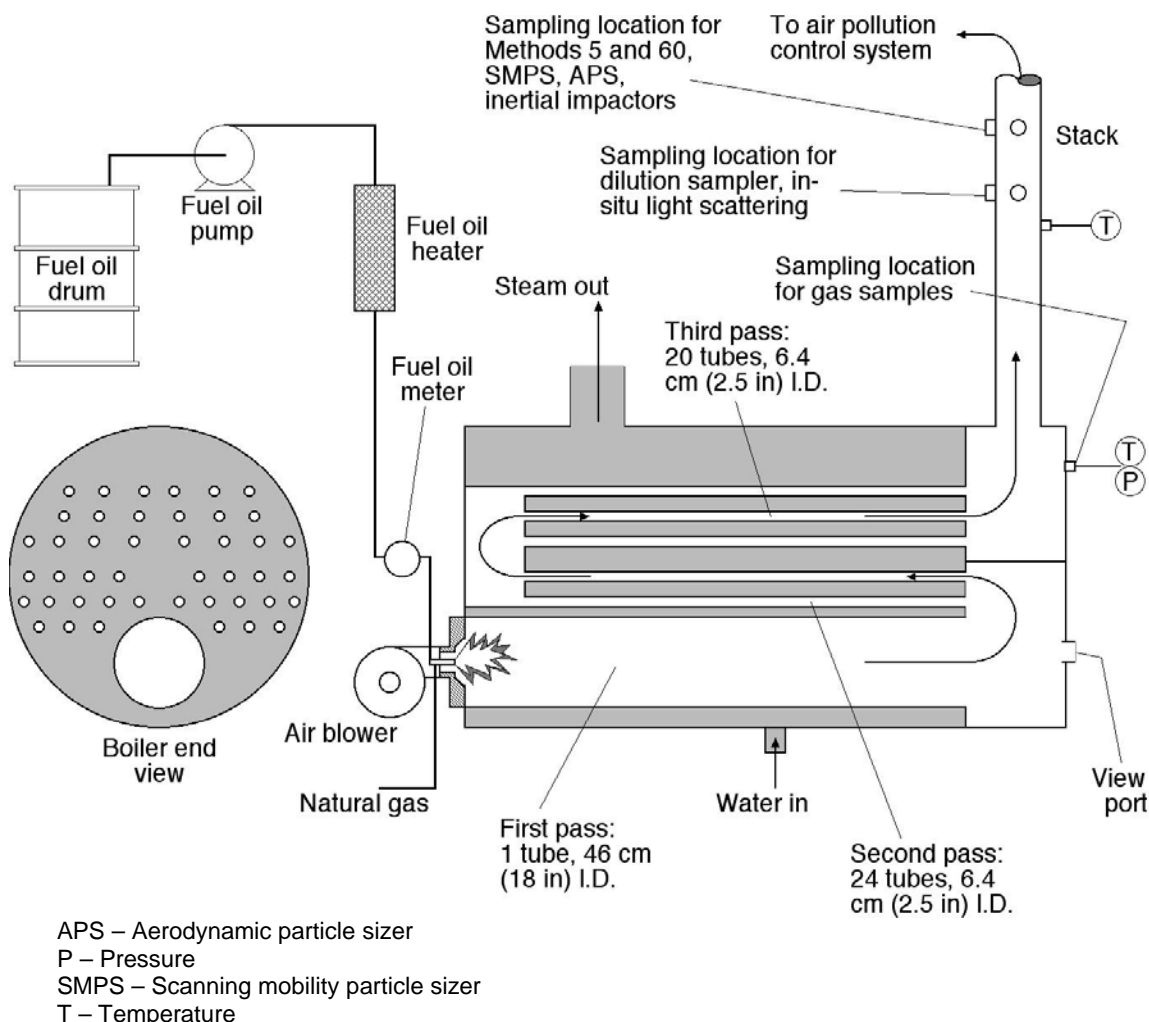


Figure 4. Schematic of NRMRL's firetube package boiler

The NAPB is equipped with several sampling ports located at the exit of the boiler. Systems of this design are characterized by a high rate of heat transfer from the combustion gases to the water, resulting in significant amounts of unburned carbon in the boiler exhaust as temperatures rapidly drop and quench the combustion reactions.

At the opposite end of the spectrum in terms of combustion gas temperatures is NRMRL's "Rainbow" horizontal tunnel furnace, shown schematically in Figure 5. This unit is less than one-tenth the size of the NAPB as measured by its fuel input rate of 200,000 Btu/hr (59 kW). The Rainbow furnace is a refractory-lined research combustor designed to simulate the time/temperature and mixing characteristics of large gas- and oil-fired combustion systems. Fuel oil and combustion air are introduced into the burner section through a variable-air swirl burner. Gas and aerosol samples are taken from the stack, where the temperature is approximately 745 °F (670K). This system generates combustion gas temperatures that are more representative of large industrial and utility

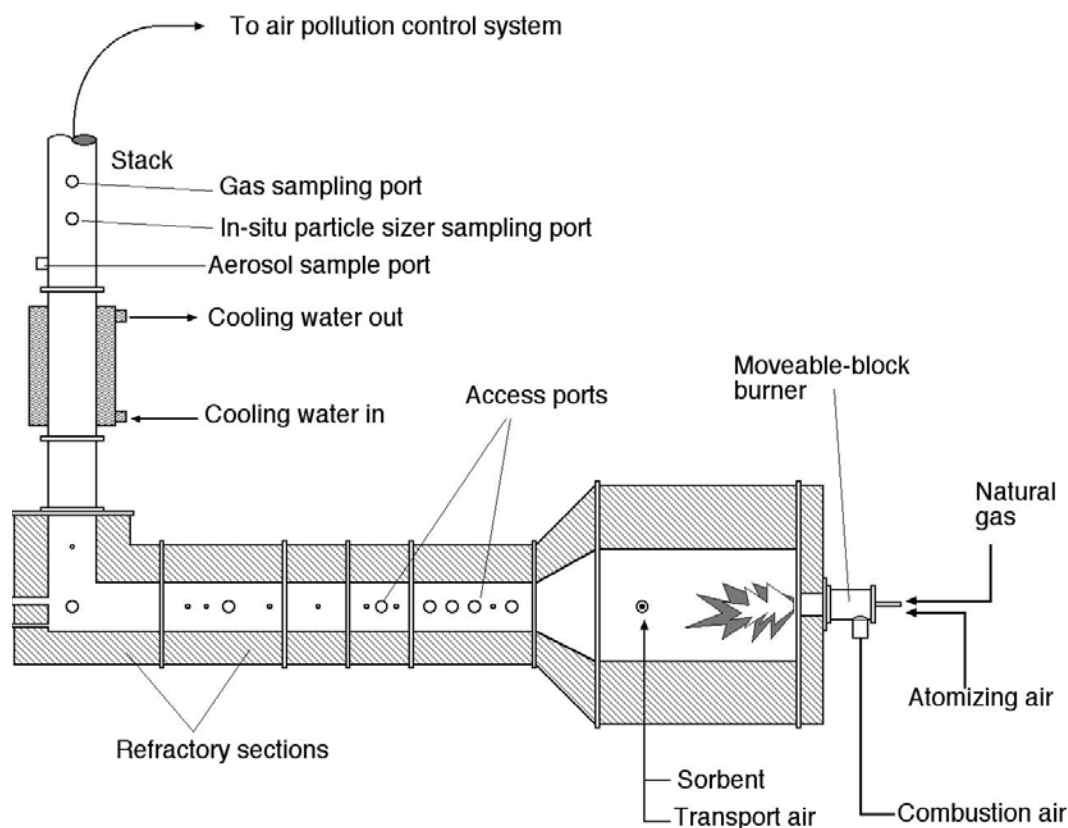


Figure 5. Schematic of NRMRL's Rainbow horizontal refractory lined furnace.

boilers compared to the temperatures in the NAPB. The Rainbow furnace is also capable of burning natural gas and a range of fuel oils.

In between the NAPB and the Rainbow in terms of combustion gas temperatures is NRMRL's Package Boiler Simulator (PBS), illustrated in Figure 6. The PBS simulates the performance of a small watertube boiler, in which the combustion gases pass through a large volume surrounded by tubes containing the fluid to be heated (usually water). The PBS, like the NAPB and the Rainbow, can burn natural gas and several types of fuel oils, including oil-water emulsified fuels. The PBS has a maximum fuel input rate of 3×10^6 Btu/hr (880 kW) and generates combustion gases that are hotter than those in the NAPB, but not as hot as those in the Rainbow.

Coal combustion experiments were conducted using a down-fired, refractory-lined furnace referred to as the Innovative Furnace Reactor (IFR) (see Figure 7) operated at 170,000 Btu/hr (50 kW). The IFR, although small, is designed to simulate the time-temperature profiles characteristic of large coal-fired boilers. The IFR is capable of burning natural gas and coal that has been pulverized to the same size range as used in

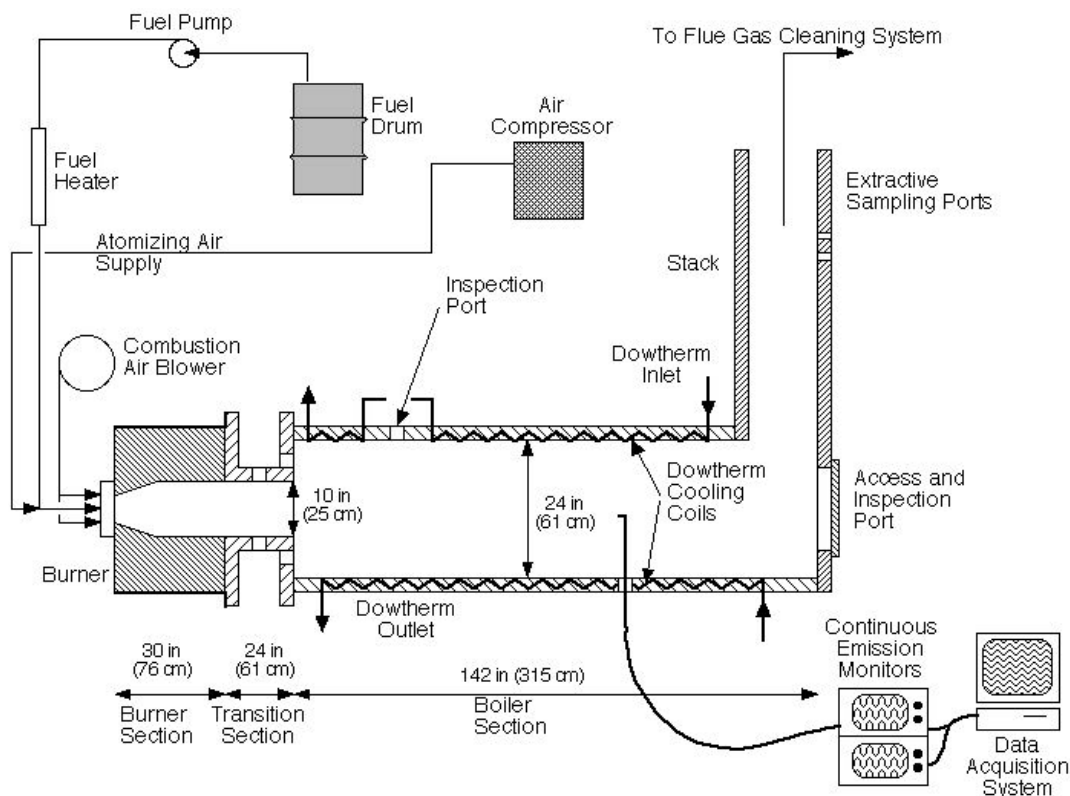


Figure 6. Schematic of NRMRL's package boiler simulator (PBS).

utility boilers. The IFR is refractory lined and generates combustion gases that are slightly cooler than large utility boilers, although levels of unburned carbon are similar to those found in full-scale utility units (Linak et al. 2000a).

Fuels

Several different fuels were used in the course of NRMRL's PM characterization tests. In addition, PM size distributions and/or compositions were measured during other NRMRL research programs characterizing emissions from different fuels, and results from those programs provide additional insight into the mechanisms governing formation of particles during fossil fuel combustion. The use of the different fuels provided NRMRL researchers the opportunity to identify both the differences and similarities among particles from different fuels.

Fuel oils are typically easier to burn than coals, due mostly to their higher volatility, their lack of significant inorganic content, and their ability to readily form small fuel particles. As fuel oils become heavier, they become more viscous, less volatile, and more difficult to effectively atomize. To efficiently burn heavy fuel oils, they must be heated, and higher pressures are required, often along with compressed air or steam, to form droplets small enough to burn to completion.

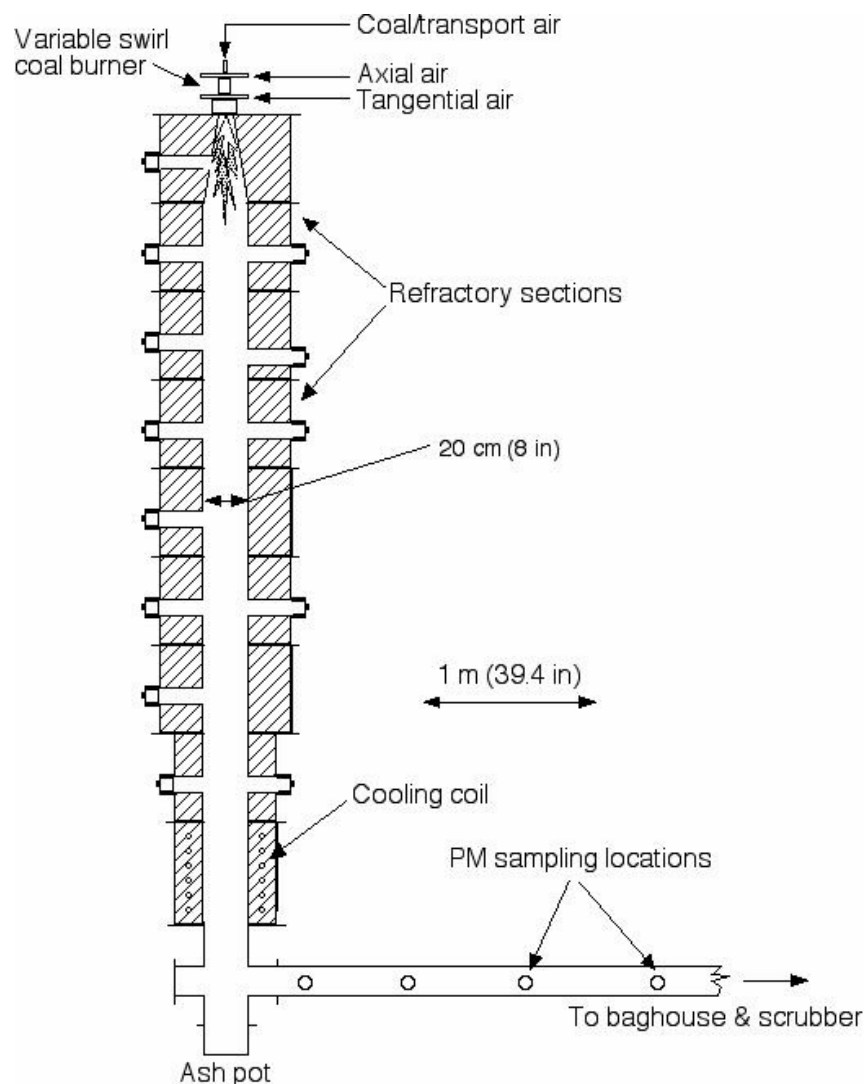


Figure 7. Schematic of NRMRL's down-fired innovative furnace reactor (IFR).

One No. 5 fuel oil and three No. 6 fuel oils were tested as part of NRMRL's initial PM characterization tests. The No. 6 fuel oils were chosen to represent a range of sulfur and metal contents, and the No. 5 fuel oil was chosen to represent a relatively high sulfur fuel oil that could be used to test the effects of changes in the combustion conditions typically experienced on a single system. (Miller et al. 1998).

In addition to the fuel oils, several U.S. coals were also burned during NRMRL's PM characterization tests. Coals were chosen to represent a range of different regions of the U.S. as well as different sulfur and metal contents. The experiments burned West Kentucky, Pittsburgh, West Virginia (Pocahontas), Ohio, and two Utah bituminous coals; Montana and Power River Basin (Wyodak) subbituminous coals; and a North Dakota

lignite. Compositions, including trace metal content, of all fuels used in the NRMRL test program are shown in Table 1.

Two other test programs conducted by NRMRL also measured PM characteristics during testing to evaluate the performance of liquid fossil fuels with different properties from conventional fuel oils. Several emulsified fuel oils and two samples of Orimulsion¹ were burned, and PM composition and size distributions were measured. Emulsified fuels contain at least two distinct materials that do not physically mix and are blended to form an emulsion. The most common emulsified fuels are water-in-oil emulsions in which small discrete droplets of water are suspended in a continuous phase of fuel oil. A more recent emulsified fuel that is being used internationally is Orimulsion, which is a bitumen-in-water emulsion in which the water is the continuous phase that contains discrete droplets of bitumen, a heavy naturally occurring petroleum fraction (Miller and Srivastava 2000, Miller et al. 2001). The presence of water in emulsified fuels has been shown to reduce emissions of total PM and NO_x under proper operating conditions, but can result in the formation of smaller particles (Miller 1996, 1998).

Each of these fuels was burned under closely controlled conditions that simulated actual industrial or utility plant operation. PM and other pollutants were measured, with the emphasis on PM, using one or more of the measurement methods noted below. In most cases, the tests were conducted several times at the same condition to evaluate variability in the measurements. Data were collected and analyzed with the goal of determining differences in PM characteristics among the different fuels and why such differences occurred.

Instrumentation and Analytical Methods

NRMRL's PM characterization studies used a variety of instruments and methods to measure combustion conditions and PM characteristics. Continuous emission monitors (CEMs) were used to measure concentrations of combustion gases, including carbon dioxide (CO₂), carbon monoxide (CO), NO_x, oxygen (O₂), SO₂, and total hydrocarbons (THCs). Signals from the CEMs were sent to a computerized data acquisition system (DAS) for continuous recording. In some cases, other process parameters, such as flue gas temperature, were also recorded using the DAS. All flue gases were treated downstream of the measurement points using air pollution control equipment for reduction of pollutant emissions.

¹ Orimulsion is an emulsified fuel produced from Venezuelan bitumen, water, and a trace amount of additives.

Table 1. Composition of fuels burned during NRMRL's PM research studies.

Content	Fuel Oils				Emulsified Fuels			Bituminous Coals				Subbituminous Coals		Lignite
	No. 5	Low S No. 6	Medium S No. 6	High S No. 6	No. 6	No. 2	Orimulsion 400	Ohio 5,6,7 Blend	Pittsburgh 8	Utah	West Kentucky	Montana	Wyodak (PRB ^a)	North Dakota
C, %	86.36	85.99	86.46	85.45	77.83	57.40	58.12	71.00	72.57	65.10	65.28	57.50	51.19	38.57
H, %	10.82	11.29	10.98	10.35	10.16	8.77	7.14	4.81	4.68	4.58	4.25	3.52	3.64	2.60
N, %	0.33	0.43	0.43	0.35	0.24	0.48	0.17	1.37	1.36	1.36	1.39	0.91	0.72	0.42
S, %	1.73	0.53	0.93	2.33	1.70	0.009	2.23	2.62	2.78	0.90	2.89	0.74	0.32	0.63
O ^b , %	0.34	1.24	0.67	0.92	10.07	2.42	3.35	8.09	7.35	12.40	11.71	15.56	12.29	12.52
Moisture, %	0.35	0.50	0.50	0.50	9.00	30.93	28.92	2.33	2.60	5.97	6.97	11.36	25.81	35.88
Ash, %	0.07	0.02	0.03	0.10	0.096	0.003	0.07	9.69	8.66	9.69	7.51	10.41	6.03	9.21
Higher Heating Value, Btu/lb														
	10,230	10,460	10,390	10,150	16,604	12,786	12,596	12,685	12,978	11,289	11,291	9526	8869	6392
Transition Metal Content, µg/g														
Cu	4	0.56	0.78	3.5	NA ^c	0.19	<0.005	NA	2.64	3.37	3	2.89	NA	NA
Fe	50	23	19	21	NA	56	22	NA	8060	2000	9210	2560	NA	NA
Ni	34	17	22	30	59	0.19	59	NA	2.19	ND ^d	6.35	2.39	NA	NA
V	180	35	70	220	440	2.77	262	NA	ND	4.25	13	4.55	NA	NA
Zn	39	4.11	3.7	74	NA	1.0	0.37	NA	4.32	ND	30.8	ND	NA	NA

^a Powder River Basin

^b Calculated by difference

^c Not available

^d Not detected

PM emissions were sampled using a variety of techniques. Standard EPA Method 5 and Method 60 sampling and analytical procedures were used to determine total PM and metal concentrations. NRMRL also uses a number of techniques for measuring particle size distributions, including a scanning mobility particle sizer (SMPS), a time-of-flight aerodynamic particle sizer (APS), a light-scattering method, and three different inertial impaction systems. These systems rely on different techniques for measuring particle size distributions, measure different size ranges, and provide data over different sampling time spans. This variety of approaches gives NRMRL researchers valuable internal verification of results and data over a broader range than would be possible with only a single instrument. The different instruments also allow NRMRL researchers to collect size-segregated samples for later analysis, providing further detailed information on the characteristics of particles that can shed light on particle formation mechanisms (Linak et al. 2000a).

Using the SMPS, APS, and light-scattering instruments, it is possible to obtain near-real time particle measurements over a range of 0.01 to 100 μm diameter. Because most current interest is in the smaller particles, only the SMPS and APS are typically used, providing particle size data over a 0.01 to 20 μm diameter range (0.01 to 1.0 μm diameter for the SMPS and 0.5 to 20 μm diameter for the APS) (Linak et al. 2000a).

Extracted samples were also collected using three different designs of cascade impactors, including an eight-stage atmospheric pressure impactor, a ten-stage Micro-Orifice Uniform Deposit Impactor (MOUDI), and a custom-made eleven-stage Berner-type low pressure impactor. The use of different impactor designs provided a wider range of data than would otherwise have been available. The atmospheric impactor collected adequate, size-segregated mass to allow elemental analysis to be conducted on the different size fractions, while the other two systems expanded the lower range of particle sizes that could be collected.

Following the initiation of collaborative studies with NHEERL, samples were also collected using a large, custom-made dilution sampler (see Figure 8). Samples were extracted from the exhaust of the combustor being used and were then passed through a cyclone designed to remove coarse ($>2.5 \mu\text{m}$) particles. To simulate the effect of a plume mixing in the ambient atmosphere, this system then diluted the particle-laden flue gases with filtered ambient air to uniformly cool the sample to approximately ambient temperatures within about 3 s. Because of the relatively low surface area associated with the coarse particle fraction, little change in particle composition or size distribution occurred due to the removal of the coarse particles. The diluted and cooled particles were then captured on a large (25.5 in diameter) Teflon coated glass fiber filter, which provided adequate collection area for the relatively large samples needed for NHEERL toxicity testing. As the program progressed, this sampler was also used to dilute flue gas samples used in direct inhalation tests by removing the filter and directing the diluted and cooled gas stream to inhalation exposure chambers.

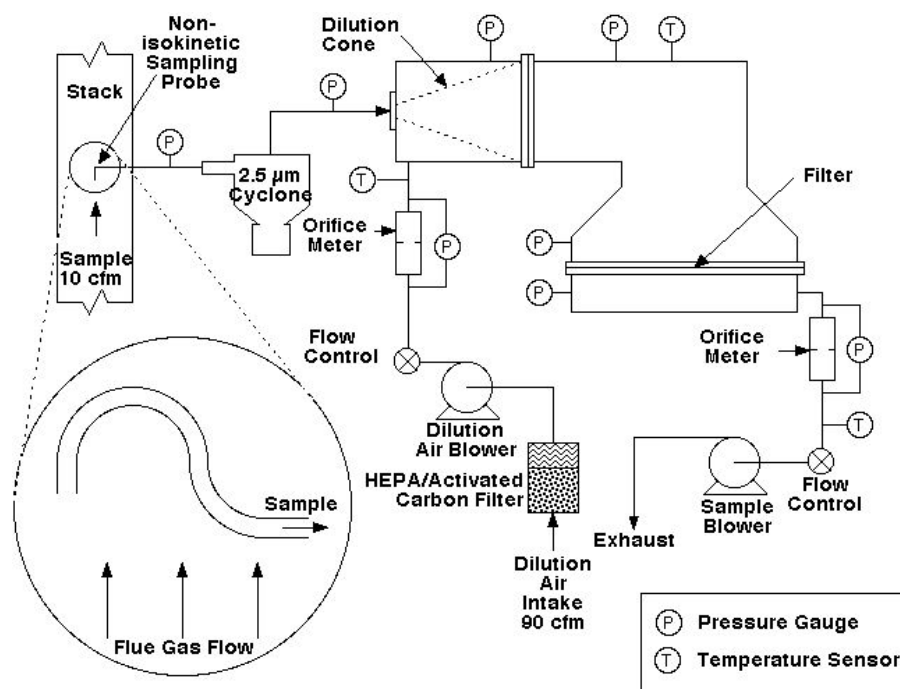


Figure 8. Schematic of NRMRL dilution sampling system.

Test Conditions

For the majority of tests, the combustion conditions were designed to simulate operating conditions typical of full-scale utility and industrial boilers. Most tests were conducted at excess air levels that were as low as possible, consistent with acceptable CO and unburned carbon in the ash. Several tests were conducted to evaluate the impacts of reducing excess air levels or to modify the fuel oil spray parameters. These tests were designed to determine whether slightly misoperated systems would significantly change the characteristics of PM compared to systems that were operated closer to optimum conditions. The greatest variation in combustion conditions occurred when the tests were conducted on combustors of different design (see descriptions above). No tests were conducted to simulate low NO_x combustion conditions such as overfire air injection, flame staging, low NO_x burners, or reburning. The nominal test conditions are presented in Table 2.

Table 2. Nominal test conditions for NRMRL's combustion tests.

Test	Fuel Oils			Emulsified Fuels		Pulverized Coals
	No. 5 and No. 6, Baseline	No. 5, Low Oil Temperature	No. 5, Low SR ^a and Low Oil Temperature	No. 2	Orimulsion	
Target Stack O ₂ , % dry	3.5	3.5	2.5	2.5	3.5	3.5
Target SR	1.2	1.2	1.1	1.1	1.2	1.2
Oil Temperature, °C	120	77	77	Ambient	40	NA

^a Stoichiometric ratio

Computer Models

In addition to the experiments, two computer models were used to assist in understanding the behavior of the fuels and their constituents. One model was designed to simulate the formation mechanisms of particles formed from vaporized materials. This model was used to predict the growth rate and size distribution of the particles, and these predictions were then compared to experimental results. The other model was used to determine the equilibrium concentrations of different chemical species formed by the fuels' trace metals in the high temperature combustion zone. As with the previous model, these predictions were compared to measurements, where possible, and were used to provide insight into what species were likely to be present in the emitted PM. The chemical species present in the PM are thought to be of importance with respect to the potential toxicity of the particles, as noted above.

Section 5

NRMRL Research Results

Primary PM From Combustion of Heavy Fuel Oils

Phase I Tests

Initial experiments were conducted with the goal of understanding how PM emissions and size-specific composition changed with changes in fuel composition and operating conditions typical of small boilers commonly used in commercial, institutional, and light industrial applications. The test results indicated that modest changes in combustion conditions did not result in significant changes in PM stack concentrations or characteristics. Reducing the fuel oil feed temperature from 120 °C to 77 °C and reducing excess air to achieve 2.5% O₂ in the stack (compared to 3.5%) changed the total PM emission rate (lb/10⁶ Btu or mg/kJ) by less than 5%. Similarly, changes in the loss on ignition (LOI) for particles larger than 2.5 µm in aerodynamic diameter were seen during the same tests. Increases of up to 18% in PM concentration (mg/m³) were noted during the same tests, and the LOI values for particles smaller than 2.5 µm in aerodynamic diameter also increased by roughly 20% (Miller et al. 1998).

The mass emission rates were different, but not significantly, for the four fuel oils burned (a No. 5 fuel oil and low, medium, and high sulfur No. 6 fuel oils). The differences in total mass emission rates correlated positively with unburned carbon levels (see Table 3). These results are consistent with particle composition, which showed high levels of carbon in the coarse particle fraction due to incomplete combustion in the relatively cold combustion environment of this firetube boiler design. The high carbon levels added significant mass to the total PM concentrations, resulting in the correlation between LOI and PM mass concentration.

Table 3. PM emission rates and emission factors and measures of unburned carbon for oils burned in NRMRL tests

Fuel type	Fuel Oils					Emulsified Fuels		
Combustor	Firetube Boiler				Refractory Lined Furnace	Firetube Boiler	Watertube Boiler Simulator	
Fuel	No. 5	Low S No. 6	Medium S No. 6	High S No. 6	High S No. 6	No. 6	No. 2	Orimulsion 400
PM, mg/m ³	197.7	219.5	243.5	183.6	93	160	3.4	160
PM, lb/10 ⁶ Btu	0.143	0.161	0.142	0.123	0.052	0.11	0.0027	0.12
PM, lb/1000 gal	21.0	24.2	21.3	18.6	7.17	15.4	0.26	12.5
Total LOI, %	NA ^a	NA	NA	NA	19.6	NA	NA	NA
Filter LOI, %	75.3	86.6	79.0	65.8	NA	NA	NA	NA
Cyclone LOI, %	95.5	96.9	93.6	90.3	NA	NA	NA	NA
Unburned carbon in fly ash, %	NA	NA	NA	NA	~0	NA	NA	NA

^a Not Available

The PSDs were consistently bimodal, with a fine mode slightly smaller than $0.1\ \mu\text{m}$ and a coarse mode near $40\ \mu\text{m}$. This indicates two particle formation processes— vaporization followed by nucleation and condensation forming the fine particle mode and mechanical processes forming the coarse mode. This is consistent with the previously published results noted earlier. These findings are also consistent with particle images viewed under a scanning electron microscope (SEM). Many of the particles from the package boiler appeared as large ($>20\ \mu\text{m}$ in diameter), porous cenospheres. These cenospheres are formed when the lighter fractions of the oil burn off, leaving the less volatile and more slowly burning char. When conditions are not hot enough or when there is not enough oxygen present, these remaining spheres composed of the heavier fractions form a char, which passes unburned out of the boiler in the form of PM. These unburned carbon cenospheres significantly increased the PM mass above what would be expected based on the fuel ash content alone (Miller et al. 1998).

The key findings from the initial phase of research are:

- Modest changes in combustion conditions, such as slightly reducing excess air and reducing the oil feed temperature, did not significantly change PM mass emissions;
- PM mass emissions from a firetube boiler do not positively correlate with oil ash content, but more closely correlate with unburned carbon levels in the ash; and
- Incomplete combustion of the carbon in the fuel results in the formation of large ($>20\ \mu\text{m}$ diameter) particles that contribute substantially to the total PM mass emission rates for these boiler designs.

As this initial study was being developed, discussions with NHEERL identified an opportunity for collaboration through providing PM samples for toxicity testing. These samples were collected from the large dilution sampler shown in Figure 8, and the particles were physically removed from the filter for later toxicological tests. Although the physico-chemical properties of the samples varied only slightly, particle samples from these initial tests showed significant differences in biological response as measured by indications of pulmonary damage following intratracheal instillation of the particles into laboratory animals. These indications were most pronounced in the fine ($<2.5\ \mu\text{m}$) particle fraction and in the oils with the highest sulfur and transition metal contents.

Phase II Tests

As a consequence of these initial studies and based on understanding of particle formation mechanisms, the research turned toward examining the effects of large changes in combustion condition by comparing particles formed in two combustion systems of significantly different design. By using a hotter furnace, more complete carbon burnout would be expected to form particles that were almost entirely in the ultrafine ($\leq 0.1\ \mu\text{m}$) fraction, since the unburned carbon that formed the larger supermicron particles would be completely combusted in the hotter unit. The smaller particles were also expected to be at least as water soluble as the fine fraction generated in the initial study and would

provide NHEERL with the ability to examine the toxicological mechanisms in more detail.

Therefore, the second set of heavy fuel oil experiments was conducted on the refractory-lined Rainbow tunnel furnace. This unit generated particles that had very little unburned carbon, in contrast to the substantial amount of carbonaceous cenospheres in the firetube boiler. The dominant particle formation route in the Rainbow furnace was through vaporization and subsequent nucleation and condensation of inorganic material. This is illustrated by the single particle size mode near 0.1 μm (see Figure 9). The smaller particles generated in the Rainbow were also found to be highly water soluble, similar to

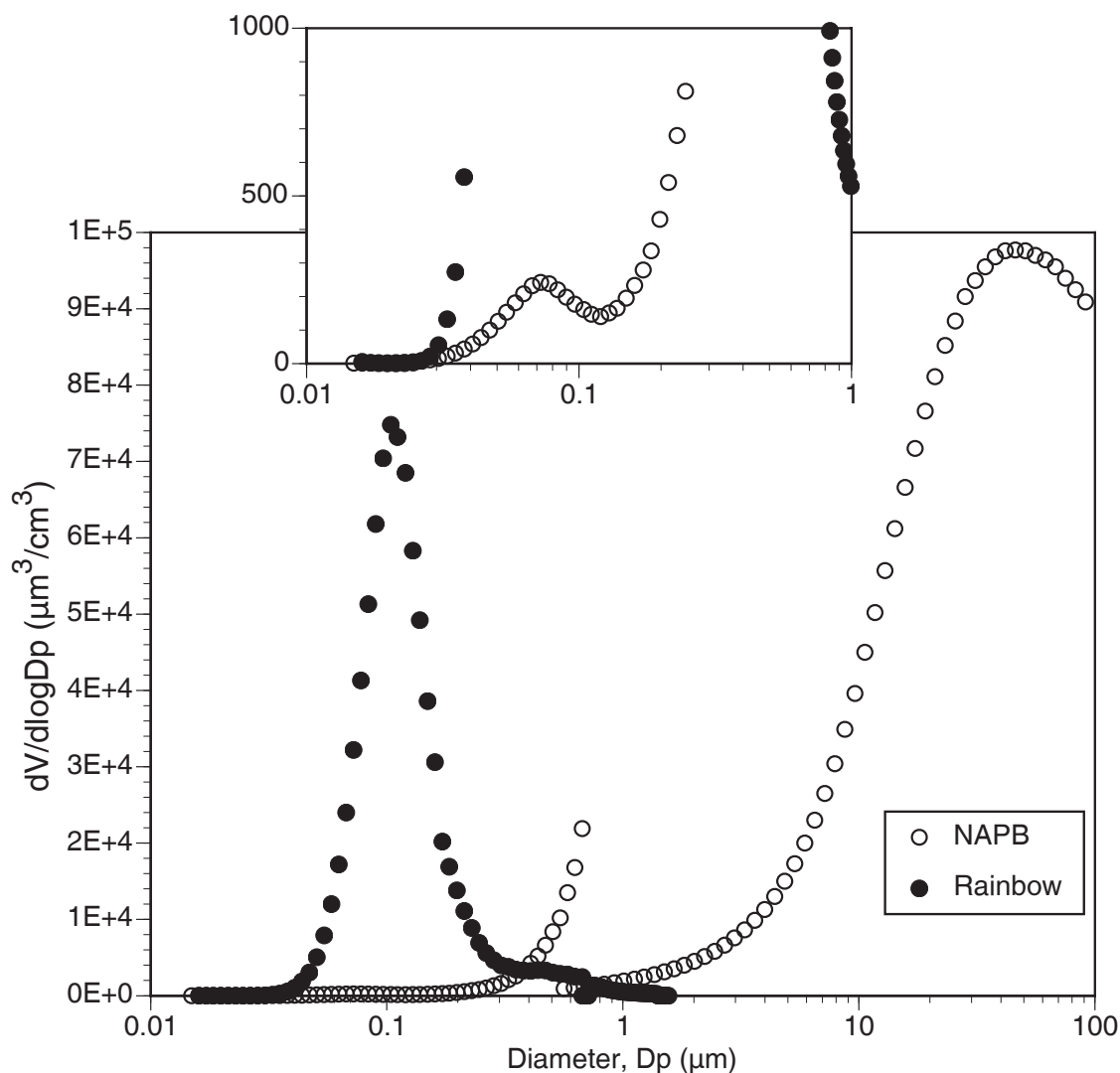


Figure 9. Particle size distributions for No. 6 fuel oil in the North American Package Boiler (open circles) and Rainbow furnace (closed circles). The inset shows details of the particle size distributions between 0.01 and 1 μm in diameter.

the fine fraction of particles from the firetube boiler. Because of the improved carbon burnout, the total PM emission rate from the Rainbow was approximately half that from the firetube boiler, even when using the same fuel at nominally similar combustion conditions (as determined by excess O₂) (Linak et al. 2000b).

The emission rates from the two combustion systems were similar to values reported from commercially operating equipment, with the firetube boiler representing small commercial and industrial boilers and the Rainbow simulating larger industrial and utility boilers. Comparing the results from these first two series of tests, it is interesting to note that more complete carbon burnout resulted in significantly less total PM mass emissions, but a higher mass of the fine particles that appear to be more bioactive.

The relationship between carbon burnout (as measured by LOI) and PM mass emissions is clearly seen in Figure 10, which also shows the relationship between fuel oil ash content and PM mass emissions for the fuels and combustors used in NRMRL's experiments. The relationship between ash content and PM emissions indicates a slight inverse relationship; as ash levels in the fuel increase, PM mass emissions decrease. It is

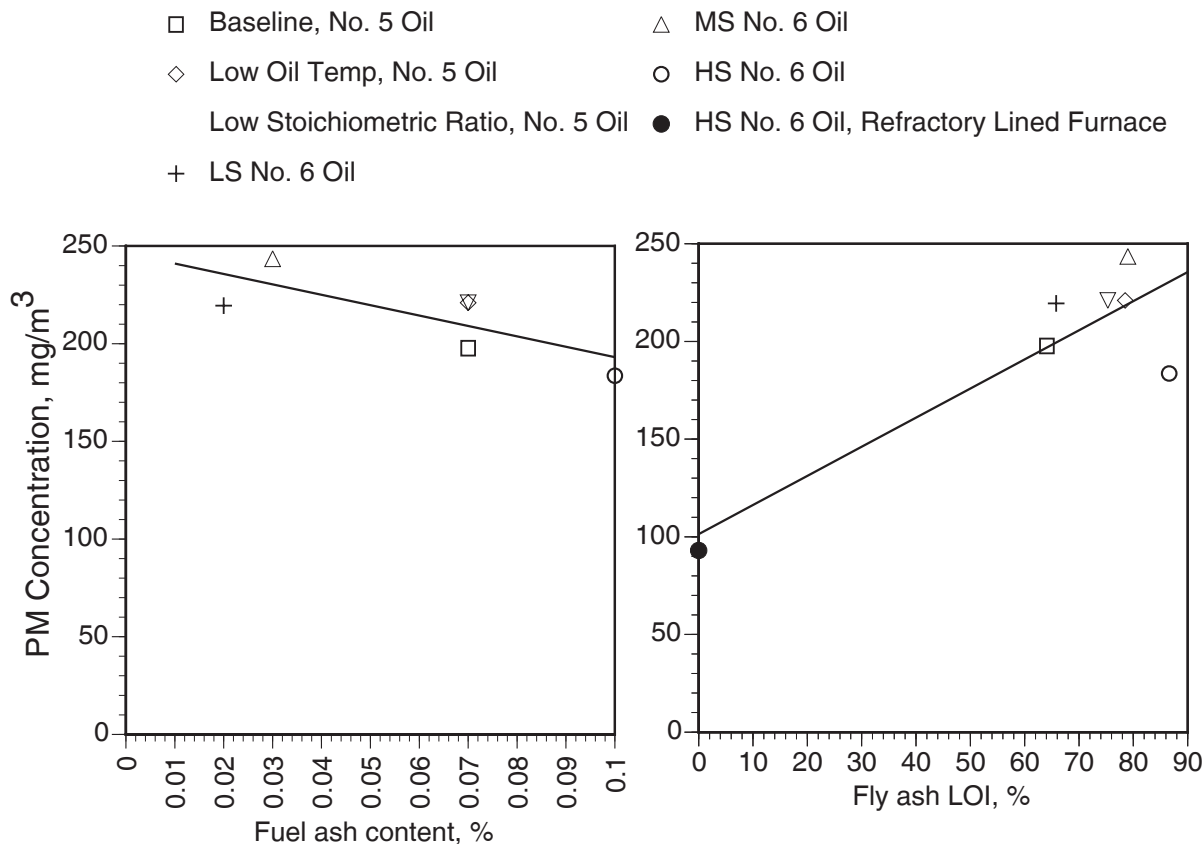


Figure 10. Stack concentrations of PM as a function of fuel ash content for the four fuel oils burned in the firetube boiler (left) and fly ash loss on ignition (right) for the four fuel oils burned in the firetube boiler and the Rainbow refractory lined furnace

unclear whether there is an underlying mechanism resulting in this relationship, but it seems unlikely that this will hold in general. For the NAPB boiler data only (i.e., ignoring the single point from the Rainbow furnace), the relationship between ash content and PM concentration shows a slightly negative correlation.

In contrast, the relationship between LOI and PM concentration is positive. Physically this makes sense because particles with high LOI contain mass that would have been converted to CO₂ under optimal conditions rather than remaining with the particles and contributing to the emitted mass. Although this positive correlation between LOI and PM is also evident from the samples taken from the firetube boiler, the most pronounced difference is between the Rainbow furnace and the data from the firetube boiler clustered in the upper right of Figure 10. This difference in PM mass emissions between the two systems clearly illustrates the impact of system design on emissions, with the hotter Rainbow generating approximately half the mass emissions compared to those from the firetube boiler.

The key findings from the second phase of the research are:

- Significant changes in combustion temperature and residence time due to different combustor designs result in substantial changes in PM characteristics and mass emissions;
- Combustion of heavy fuel oil under conditions simulating large industrial and utility boilers generates a nearly unimodal submicron PSD; and
- The submicron particles contain metals and sulfur that are largely in water soluble form, in contrast to the supermicron fraction of particles that contains less soluble thiophenic sulfur and metal species.

The level of unburned carbon also appears to influence the chemical species that are formed. Detailed examination of the particles from the NAPB indicate that approximately 50% of the sulfur in the particles is not oxidized, although essentially all of the sulfur in the PM collected from the Rainbow furnace is in the form of sulfates (SO₄) (Huffman et al. 2000, Pattanaik et al. 2000). The form of sulfur is significant, since the sulfate form is much more soluble in water than the unoxidized organic (thiophenic) form of sulfur. Much of the sulfate in these submicron particles is combined with metals, resulting in metals with relatively high solubility in water. As noted earlier, one of the characteristics of particles from heavy fuel oil that is suspected of leading to adverse health effects is the presence of water-soluble transition metals, and metal sulfates are much more water-soluble than most other metal species that are formed in combustion systems. The combination of transition metals and high sulfate levels indicates that the Rainbow PM is likely to contain much higher levels of water-soluble transition metals than the PM from the NAPB, even though both are generated by combustion of the same fuel.

Data from Other Studies

In addition to the conventional heavy fuel oils, two water-in-oil emulsified fuels and Orimulsion, a bitumen-in-water fuel, were also tested under other programs. PM size distributions and mass emissions were tested during these programs and provide additional information of relevance here. For the emulsified fuels tested, the presence of water in the fuel changed the way the fuels burned and resulted in noticeable changes in PM emissions and size distributions. The water in the emulsified fuel oils created “microexplosions” as the fuel is rapidly heated, thereby forming much smaller fuel droplets than could be formed by the mechanical processes of the nozzle. These smaller droplets burn more quickly, thereby reducing the amount of unburned carbon and reducing both the mass of PM emissions and the size of the emitted particles (Miller et al. 2001, Miller 1996). Even though the physical arrangement of Orimulsion is different from the water-in-oil emulsified fuel oils, the results were very similar when compared to a non-emulsified fuel oil. This is most likely due to the small size (8-20 μm diameter) of the bitumen droplets in the Orimulsion, which is much smaller than the fuel oil droplets generated by the oil nozzle (Miller and Hall 2000). The net effect of the microexplosions and subsequent smaller fuel droplets is to reduce the time needed to volatilize and combust the fuel. This reduces the impact of rapid temperature drop in systems such as the firetube boiler and results in particles with lower unburned carbon and higher fractions of submicron particles compared to non-emulsified fuels burned under similar conditions.

Further Evolution of Research Directions

Given the successful generation, sampling, and instillation of particles in these first two series of tests, the research then moved forward along two different, but complementary, routes. The physico-chemical characterization studies of heavy fuel oil were essentially complete, but there was substantial interest in expanding the collaboration on determining toxicity by providing a source of particles for joint NMRML-NHEERL studies of direct inhalation of the particles by animals. This work has begun with initial tests using heavy fuel oil. This route of research is anticipated to continue for the foreseeable future, with the emphasis on toxicological rather than physicochemical characterization. Results from these collaborative studies are still being analyzed, but the capability to generate well characterized, real-world particles for real-time inhalation exposure studies has been demonstrated and can be applied to other source types as research needs dictate.

The second route of research stemming from the original heavy fuel oil studies was testing of pulverized coals. Although there has been much more research conducted to characterize PM generated by the combustion of pulverized coal, no physico-chemical characterization studies were known to have been conducted with the goals of quantifying the presence of water soluble transition metals and generating well-characterized primary PM samples for toxicity studies aimed at better understanding the causal mechanism of health damage associated with exposure to ambient PM_{2.5}.

Primary PM From Combustion of Coals

Nine different U.S. coals were burned during NRMRL's PM characterization tests. These coals were chosen to represent different regions of the U.S. and have different sulfur and trace element contents (see Table 1) as well as different ash chemistry. The initial tests focused on particle size, mass, and composition measurements for the coals burned in the down-fired IFR.

PM concentrations generated by the combustion of coal were much higher than for the fuel oils, as shown in Table 4. This is expected because of the significantly higher amount of inorganic ash present in the coal (8-20%) compared to the fuel oils (usually much less than 1%). Uncontrolled mass concentrations for the coals tested were over 20 times higher than those for the heavy fuel oil, which is similar to the ratio of inorganic ash contents of the coals versus the fuel oils. However, most of the coal PM mass is in the larger ($>5\ \mu\text{m}$ diameter) size fractions, with only about 4 to 7% of the total PM mass associated with $\text{PM}_{2.5}$. The unburned carbon values measured in EPA's experiments were slightly higher than, but not atypical of, many utility-scale boilers and considerably less than the LOI values for the PM from heavy fuel oil burned in the NAPB (Linak et al. 2000a). However, because of the much higher levels of inorganic material in coal compared to that in heavy fuel oil, it can be misleading to directly compare fractions of unburned carbon or LOI for the two fuel types. For instance, 5% unburned carbon for a coal-generated PM may translate into more total mass of unburned carbon than 80% unburned carbon for PM from the combustion of heavy fuel oil. The much higher inorganic content in coal also results in unburned carbon having a much lower effect on PM mass emissions for coal than for oil, since coal PM mass emission rates are dominated by the inorganic material present in the fuel.

Table 4. PM emission rates and emission factors and measures of unburned carbon for coals burned in NRMRL tests.

Fuel Type	Bituminous Coals				Subbituminous Coal		Lignite
Fuel	Ohio 5,6,7 Blend	Pitts- burgh 8	Utah	West Ken- tucky	Montana	Wyodak (PRB ^(a))	North Dakota
PM, mg/m^3	4477	3565	4323	3807	4374	3441	5582
PM, $\text{lb}/10^6\ \text{Btu}$	3.70	2.71	3.32	3.00	3.30	2.63	6.02
PM, lb/ton	95.2	70.3	74.9	67.9	62.8	46.6	77.0
Unburned carbon in fly ash, %	NA ^a	NA	10.9	10.2	0.5	NA	NA

^a Not available

NRMRL's experimental results demonstrate some of the different mechanisms involved in particle formation during coal combustion. Figure 11 presents typical particle size distributions for several of the coals tested. The three distinct modes indicate different formation mechanisms. The smallest mode occurs near $0.1\ \mu\text{m}$ in diameter and is due to the vaporization and subsequent nucleation and accumulation similar to that in the

ultrafine particles from heavy fuel oil combustion. These particles tend to be enriched in metals that have volatilized and nucleated and to have high levels of sulfates. The second mode occurs between 0.8 and 2.0 μm in diameter and has not been commonly identified in previous studies. This mode is believed to be composed of fragments of ash particles originally contained within the pulverized coal particles. The third mode begins near 10 μm diameter and is formed largely by coalescing inorganic material that is produced as the carbonaceous coal char burns away. The two largest modes have similar composition, indicating similar mechanical mechanisms of formation (Linak et al. 2001, Shoji et al. 2000). The similarity in composition supports the hypothesis that the 0.8-2 μm particles were originally part of the larger ($>10 \mu\text{m}$) particles, which fragmented to form the

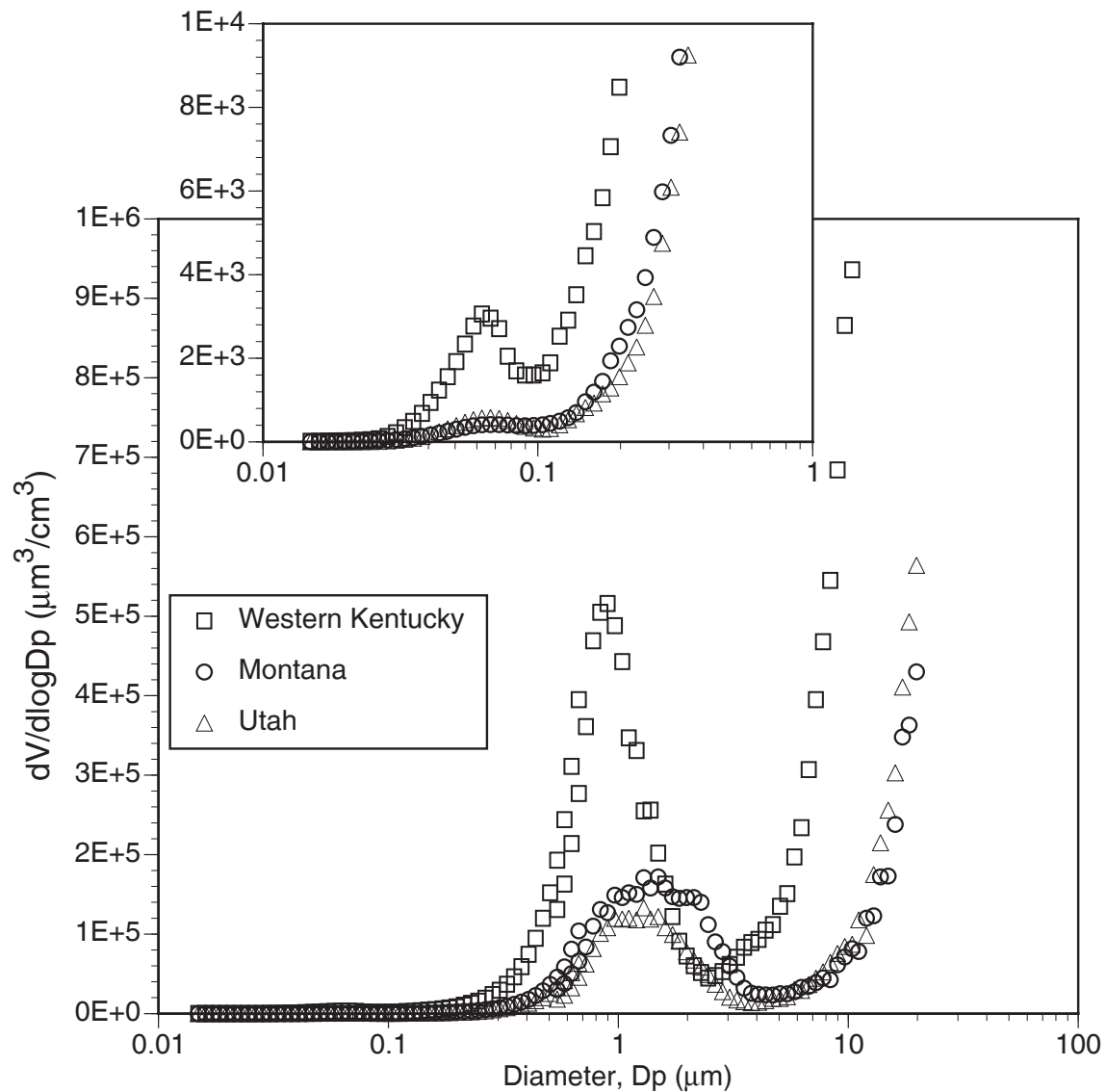


Figure 11. Particle size distributions for three coals burned in NRMRL tests.

0.8-2 μm particles. Both these larger modes significantly differ in composition from the submicron mode.

As is the case for PM from heavy fuel oils, the particles larger than 1 μm are formed by primarily mechanical means and will contain metals in forms that are tightly bound physically and chemically. This will result in water solubility that is significantly lower than that seen for PM from heavy fuel oils. The submicron particles, formed via vaporization, nucleation, and condensation, will be composed in part of metal and other sulfates that have a much higher solubility in water, and are therefore expected to have a higher level of bioavailability.

Figure 12 illustrates the relationships between coal ash content and PM mass concentrations, and LOI and PM mass concentrations. Note the contrast between these relationships and those for the heavy fuel oils (see Figure 10). For coal, the fuel ash content has a significant effect on PM concentrations, while LOI has minimal, if any, effect. As noted above, this is due to the much higher ash content in coals that overwhelms any significant effect from LOI.

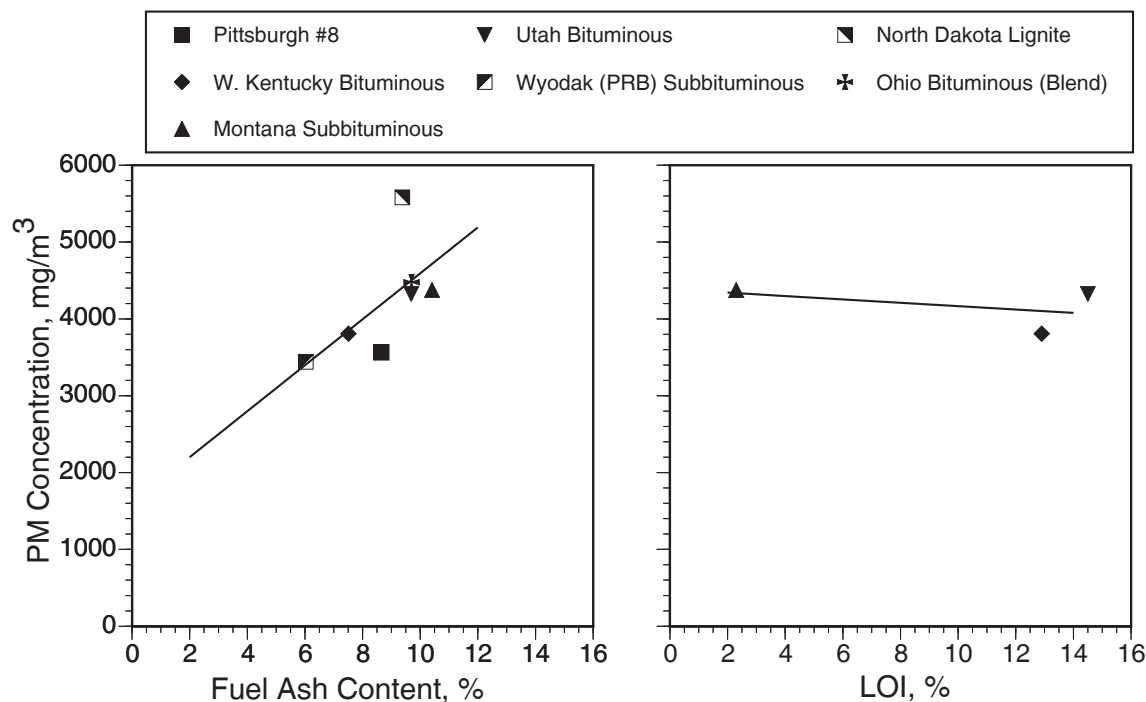


Figure 12. Stack concentrations of PM as a function of fuel ash content (left) and fly ash loss on ignition (right) for the seven coal burned in the innovative furnace reactor.

The presence of the “fine fragmentation” mode between 0.8 and 2.0 μm means that the $\text{PM}_{2.5}$ from coal combustion will be composed of particles formed by different mechanisms, and with different chemical compositions. The fine fragmentation mode

makes up the majority of coal-generated PM_{2.5} mass and has characteristics similar to the coarse (>2.5 µm) particle fraction. These particles will contain significant amounts of silica and alumina compounds that tie up many of the other trace elements, including the transition metals. On a per-unit-mass basis, therefore, PM_{2.5} from coal combustion is likely to contain less water-soluble transition metals compared to PM_{2.5} from heavy fuel oil. Even so, there will remain in coal-generated PM an ultrafine fraction that is expected to be more similar in composition and physical characteristics, and possibly in toxicological characteristics, to the ultrafine fraction in PM_{2.5} from heavy fuel oil combustion.

As was the case for PM from heavy fuel oil, these results emphasize that particle size and composition are a consequence of the formation processes. The larger particles (>0.8 µm) are formed by processes that do not involve vaporization and are therefore less likely to undergo significant chemical change. On the other hand, the ultrafine particles that do vaporize are more likely to undergo the same types of chemical reactions that favor the formation of water soluble metal sulfates.

The hypothesis that the submicron fraction of the coal generated PM may be more bioactive than the larger particle fractions has led NRMRL researchers to begin efforts to collect larger quantities of these particles. Because they make up such a low percentage of the total particle mass, however, such collection requires different particle generation and collection techniques. One approach is to begin with micronized coal, which is ground to a much finer size (~ 5 µm) than standard pulverized coal (~ 70 µm). This approach is expected to generate a substantially higher fraction of the ultrafine particles of interest, making collection of significant quantities of these particles for NHEERL toxicity studies much more efficient. Initial efforts in this area are promising and are ongoing at the writing of this report.

The key findings from this segment of the NRMRL research program are:

- A previously unreported particle mode between 0.8 and 2.0 µm contributes to the mass of PM_{2.5} from the combustion of pulverized coal;
- The composition of particles in this “fine fragmentation” mode is similar to that of the coarse mode particles, suggesting that the mode is formed by coarse ash particles that fragment during the combustion process. The composition also suggests that these particles will have metals with relatively low water solubility and therefore relatively low bioavailability; and
- The ultrafine fraction of coal-generated particles has composition similar to that of the ultrafine mode of particles from heavy fuel oil combustion, suggesting that the pulmonary toxicity of ultrafine particles from coal combustion may be similar to the heavy fuel oil ultrafine particles.

Model Predictions

In addition to the experimental program, NRMRL researchers also used computer models to help explain the behavior and speciation of particles. These models were used to simulate the major chemical and physical processes governing the formation and speciation of particles and to provide data to which the experimental results could be compared. This approach provided guidance in interpreting the experimental results and was especially useful in gaining a better understanding of the metal species likely to be present in the ultrafine PM.

Chemical Equilibrium Modeling

Chemical equilibrium calculations allow one to identify chemical species that will form with adequate time at a given temperature. While they do not account for the effects of incomplete mixing or chemical reactions that do not have adequate time to go to completion (kinetics), equilibrium results can be used to determine what chemical species are likely to be present in a given environment and how changes in temperature or presence of other compounds can influence the speciation in the flue gases.

Thermochemical predictions for a simulated heavy fuel oil were determined using the Chemical Equilibrium Analysis (CEA) computer code for calculating complex chemical equilibrium compositions (McBride et al. 1993) with thermochemical data taken from the literature (see Linak et al. 1999, 2000b). Of interest is the predicted partitioning between vapor and condensed phases as well as elemental speciation. Using experimental data from NRMRL tests (Miller et al. 1998), CEA predicted that seven inorganic elements of potential interest to toxicologists were likely to form vapor phase species in the high temperature regions of combustion systems. All seven of these elements were also predicted to form sulfates at temperatures typical of exhaust stacks (Linak et al. 1999, 2000b). These results were consistent with the study of Huffman et al. (2000) that analyzed for several species in the fine and coarse fractions of oil-generated PM samples collected during the NRMRL experiments. Taken together, the computational and analytical results demonstrate that the formation of water soluble sulfate species is favored by the conditions present in large industrial and utility boilers.

Aerosol Nucleation and Coagulation Modeling

In addition to modeling the chemical processes, NRMRL researchers also used a multi-component aerosol simulation (MAEROS) code (Gelbard and Seinfeld 1980) to model the physical evolution of particle sizes. The purpose of these calculations was to determine whether the experimental data were consistent with the calculated predictions to support the interpretation of the experimental results. A secondary objective was to examine the effects of particle coagulation on particle size distributions, specifically to evaluate how changes in the vaporized inorganic material would impact PSDs.

Beginning with initial conditions based on NRMRL experimental results, MAEROS predicted PSDs similar to those measured during the heavy fuel oil tests. The

consistency of the model and experimental results indicated that NRMRL's interpretation of the particle formation mechanisms based on the experimental data is reasonable (Linak et al. 1999, 2000b).

Section 6

Summary and Implications

Summary

In summary, NRMRL's combustion PM research has found the following:

- Increased unburned carbon results in increased PM mass emissions and increased particle size when burning heavy fuel oil.
- Use of emulsified fuel oils reduces both the PM mass and the particle size compared to a non-emulsified fuel oil.
- Unburned carbon does not affect PM mass emissions or particle size distributions nearly as strongly for coal as for heavy fuel oil.
- For all fossil fuels tested, the submicron particles tend to have higher concentrations of metals and sulfates than particles larger than 1 μm in diameter.
- The water solubility of metals is significantly higher for the total PM from heavy fuel oils than for the total PM from pulverized coal, although the similar compositions of the ultrafine fractions of both fuels suggests the difference for this fraction is much smaller.
- A fine fragmentation mode between 0.8 and 2.0 μm exists in PM generated from the combustion of pulverized coal. The particles in this mode are of similar composition to the particles in the coarse ($>2.5 \mu\text{m}$) mode.

Implications

Particle composition varies considerably with size, with potentially significant implications for particle toxicity. NRMRL's research, consistent with previous work, has identified significant variation in particle composition as a function of particle size. The submicron particle fractions were consistently composed of metal and other sulfates that are highly water soluble, meaning that they are more likely to interact with biological tissues when inhaled. The formation mechanisms that generate these particles govern both size and composition. Therefore, the question of whether size or composition plays a dominant role in causing adverse health effects may be inappropriate, since the two (size and composition) cannot be separated in real-world systems. It may be more relevant to focus on particles with similar formation processes rather than on particles with specific characteristics that cannot be naturally separated. In short, multiple mechanisms are involved in the formation of $\text{PM}_{2.5}$ from combustion sources, and these mechanisms will directly impact the role of particles in causing adverse health effects.

The design and operation of a source can result in significant changes in the physico-chemical and toxicological characteristics of the particles generated. This finding has scientific and potentially regulatory implications. In the context of toxicological research, more emphasis needs to be placed on how particle samples are generated and collected. PM toxicological studies often do not adequately describe the source characteristics, including system design, the conditions at which the system is running, or the methods used to extract particle samples. PM from heavy fuel oil, as

demonstrated here, is not a homogeneous material with consistent characteristics. In order to develop an adequate understanding of the health effects associated with PM and the causal mechanisms leading to those effects, studies must provide enough information to allow the reader to understand the representativeness of the particles used in the tests.

From a regulatory perspective, these results may eventually be used to identify source types that have the potential for emitting particles having characteristics closely associated with health risk. As additional understanding is gained regarding links between health effects and particle characteristics, it may someday be possible to develop regulatory approaches to reduce PM emissions from a more limited range of source types or to minimize emissions of particles with certain characteristics. If enough information on adverse health effects due to water-soluble ultrafine particles is developed, for instance, limits on emissions of these particles may replace or supplement limits on total mass emissions.

Section 7

Future Directions

NRMRL's research to characterize primary particles from the combustion of pulverized coal and heavy fuel oils has been completed. There remain numerous research opportunities in the broader area of combustion-generated particles, which will be followed as appropriate. Immediate efforts will focus on characterizing emissions from small off-road diesel engines, which will involve more organic analysis, as compared to the significant levels of inorganic analysis conducted for the previous studies. Several efforts associated with the collaborative studies linking the physicochemical properties of combustion-generated particles to measures of toxicity during direct inhalation exposures will continue. This area of work shows considerable promise for generating data that can be used to better understand the links between sources and adverse health effects.

The capabilities developed during the work described in this report will continue to generate state of the art research. NRMRL's flexible and unique facilities, in combination with ORD's on-site expertise, provide unique opportunities for leading edge multidisciplinary research in PM, air toxics, and other air programs.

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Section 8

Publications from NRMRL's Combustion-Generated PM Research Program

The 10 articles listed below represent key publications generated from the work described above (NRMRL authors noted in boldface). In addition to these publications, an additional 12 papers were prepared and presented at technical conferences between 1997 and 2002.

Huffman, G.P., Huggins, F.E., Shah, N., Huggins, R., **Linak, W.P., Miller, C.A.,** Pugmire, R.J., Meuzelaar, H.L.C., Seehra, M.S., and Manivannan, A. (2000). "Characterization of fine particulate matter produced by combustion of residual fuel oil," *Journal of the Air & Waste Management Association*, Vol. 50, 1106-1114.

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Section 9

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15. SUPPLEMENTARY NOTES Project Officers are C. Andrew Miller, MD E-305-01, phone (919) 541-2920, and William P. Linak, MD E-305-01, phone (919) 541-5792.		
16. ABSTRACT <p>Researchers at the U.S. Environmental Protection Agency's Office of Research and Development (ORD) have conducted a series of tests to characterize the size and composition of primary particulate matter (PM) generated from the combustion of heavy fuel oil and pulverized coal. These tests, conducted at ORD's National Risk Management Research Laboratory (NRMRL) in Research Triangle Park, NC, burned four heavy fuel oils and seven coals in three small combustion systems and measured size distributions and composition of the particles formed in the combustion process. The research found that, for heavy fuel oils, particle composition and size are dependent upon the combustion environment in the combustor. In the coolest test unit, unburned carbon in the fly ash was very high (70-90% by mass), and PM mass emissions were also high, with the majority of the mass being in the coarse (>2.5 µm in aerodynamic diameter) size range. In the hottest test unit, the PM mass emissions were approximately 50% of those from the coolest unit, unburned carbon levels were approximately zero, and the entire PM mass was in particles smaller than 1 µm in aerodynamic diameter. For coal, the NRMRL research identified a previously unreported trimodal particle size distribution, with an ultrafine (~ 0.1 µm in aerodynamic diameter) mode, a coarse (>5 µm in aerodynamic diameter) mode, and a central mode of particles between 2 and 4 µm in aerodynamic diameter. The central mode has a composition similar to the coarse mode, but significantly different from the ultrafine mode. It is hypothesized that the composition of the ultrafine coal particle fraction is similar to the fine particle fraction in heavy fuel oil, which has been shown to generate increased toxicological responses following pulmonary exposure in laboratory animals. These findings may have implications for future PM control strategies, given the influence of operating conditions and the water-soluble composition of the smallest particle fractions of PM from metal-bearing fossil fuels.</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Combustion Mortality Morbidity Fuel Oil Coal Particle Size Distribution	Pollution Control Stationary Sources	13B 12B 05K 06E 11H, 21D 08G 14G
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